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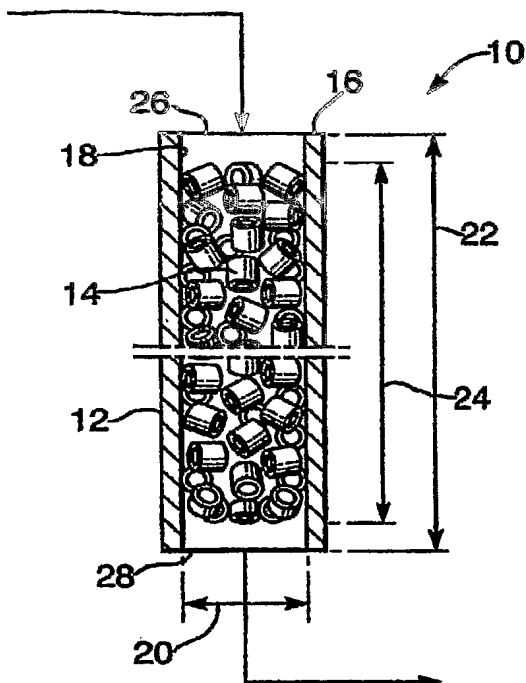
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(54) Title: A REACTOR SYSTEM AND PROCESS FOR THE MANUFACTURE OF ETHYLENE OXIDE



(57) Abstract: A reactor system for the oxidation of ethylene to ethylene oxide. The reactor system includes a reactor tube that contains a packed bed of shaped support material that can include a catalytic component. The shaped support material has a hollow cylinder geometric configuration. The reactor system has specific combinations of reactor tube and catalyst system geometries.

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A REACTOR SYSTEM AND PROCESS FOR THE
MANUFACTURE OF ETHYLENE OXIDE

The invention relates to reactor systems. Another aspect of the invention relates to the use of reactor systems in the manufacture of ethylene oxide.

Ethylene oxide is an important industrial chemical used as a feedstock for making such chemicals as ethylene glycol, ethylene glycol ethers, alkanol amines and detergents. One method for manufacturing ethylene oxide is by the catalyzed partial oxidation of ethylene with oxygen. In this method, a feedstream containing ethylene and oxygen is passed over a bed of catalyst contained within a reaction zone that is maintained at certain reaction conditions. Typically, the ethylene oxidation reactor is in the form of a plurality of parallel elongated tubes that are filled with supported catalyst particles to form a packed bed contained within the reactor tubes. The supports may be of any shape, such as, for example, spheres, pellets, rings and tablets. One particularly desirable support shape is a hollow cylinder.

One problem encountered with the use of a packed bed of hollow cylinder supported catalyst particles in an ethylene oxidation reaction zone is the difficulty in having a proper balance between the pressure drop that occurs across the catalyst bed during the operation of the ethylene oxide process and the catalyst bed packing density. Catalyst performance is generally improved with increased catalyst packing density in the ethylene oxidation reaction tubes; however, undesirable increases in pressure drop across the reactor generally accompany an increased catalyst packing density.

It is desirable in the manufacture of ethylene oxide by the partial oxidation of ethylene to utilize a reactor system

with a packed catalyst bed having a high packing density but with minimized pressure drop across the packed catalyst bed.

It is, thus, an object of this invention to provide a reactor system suitable for use in the catalytic partial oxidation of ethylene oxide, which has a packed catalyst bed having a high packing density but still provides for a suitably low-pressure drop during its operation.

Other aspects, objects, and the several advantages of the invention will become more apparent in light of the following disclosure.

In one aspect, the invention may be defined as providing a reactor system comprising:

an elongated tube having a tube length and a tube diameter which define a reaction zone; wherein contained within the reaction zone is a packed bed of shaped support material; and wherein the shaped support material has a hollow cylinder geometric configuration defined by a nominal length, a nominal outside diameter and a nominal inside diameter such that the ratio of the nominal length to the nominal outside diameter is in the range of from 0.5 to 2, and further such that

when the tube diameter is less than 28 mm, the ratio of the nominal outside diameter to the nominal inside diameter exceeds 2.3, and the ratio of the tube diameter to the outside diameter is in the range of from 1.5 to 7, and

when the tube diameter is at least 28 mm, the ratio of the nominal outside diameter to the nominal inside diameter exceeds 2.7, and the ratio of the tube diameter to the outside diameter is in the range of from 2 to 10.

In another aspect, the invention may be defined as providing a reactor system comprising:

an elongated tube having a tube length and a tube diameter which define a reaction zone; wherein contained

within the reaction zone is a packed bed of shaped support material; and wherein the shaped support material has a hollow cylinder geometric configuration defined by a nominal length, a nominal outside diameter and a nominal inside diameter such that

the ratio of the nominal length to the nominal outside diameter is in the range of from 0.5 to 2, and

the ratio of the nominal outside diameter to the nominal inside diameter provides a positive test result, as defined hereinafter, and further such that

the ratio of the tube diameter to the nominal outside diameter is in the range of from 1.5 to 7, when the tube diameter is less than 28 mm, and in the range of from 2 to 10, when the tube diameter is at least 28 mm.

Herein, "positive test result" is defined by a decrease of the quotient of a numerical value of the pressure drop per unit length of the packed bed and a numerical value of the packing density, which numerical values are obtained by testing the packed bed in a turbulent flow of nitrogen gas at a pressure of 1.136 MPa (150 psig), relative to a comparison quotient of numerical values obtained in an identical manner, except that the hollow cylinder geometric configuration of the same support material is defined by a nominal outside diameter of 6 mm and a nominal inside diameter of 2.6 mm, when the tube diameter is less than 28 mm, and a nominal outside diameter of 8 mm and a nominal inside diameter of 3.2 mm, when the tube diameter is at least 28 mm, and further by a ratio of the nominal length to the nominal outside diameter of 1.

According to another aspect of the invention, a process for manufacturing ethylene oxide includes introducing into a reactor system according to this invention a feedstock comprising ethylene and oxygen and withdrawing from the

reactor system a reaction product comprising ethylene oxide and unconverted ethylene, if any, wherein within the reaction zone is the supported catalyst system that comprises a catalytic component supported on the shaped support material having a hollow cylinder geometric configuration.

Further, the invention provides a method of using ethylene oxide for making ethylene glycol, an ethylene glycol ether or an 1,2-alkanolamine comprising converting ethylene oxide into ethylene glycol, the ethylene glycol ether, or the 1,2-alkanolamine, wherein the ethylene oxide has been obtained by the process for preparing ethylene oxide according to this invention.

As used herein, in the context of the hollow cylinder geometric configuration the terms "inside diameter" and "bore diameter" have the same meaning and have been used herein interchangeably. Also, as used herein, the terms "carrier" and "support" have the same meaning and have been used herein interchangeably.

FIG. 1 depicts certain aspects of the inventive reactor system that includes a tube having a length that is packed with a packed bed comprising the shaped support material of a catalyst system;

FIG. 2 depicts the shaped support material of the catalyst system of the invention and which has a hollow cylinder geometric configuration and the physical dimensions that characterize the shaped support material;

FIG. 3 is a schematic representation of an ethylene oxide manufacturing process which includes certain novel aspects of the invention;

FIG. 4 presents data on the changes ("C (%)") in pressure drop ("% DP") and tube packing density ("% TPD"; "% TPD*" represents duplicate data) resulting from the use of various sizes (outer diameters) of hollow cylinder support

material with different length-to-diameter ratios ("L/D") in a 39 mm diameter reactor tube relative to the use of a standard 8 mm hollow cylinder support material;

FIG. 5 presents data on the changes ("C (%)") in pressure drop ("% DP") and tube packing density ("% TPD"; "% TPD*" represents duplicate data) resulting from the use of various sizes (outer diameters) of hollow cylinder support material having a nominal length-to-diameter ratio of 1.0 and different bore diameters ("BORE", specified in mm) in a 39 mm diameter reactor tube relative to the use of a standard 8 mm hollow cylinder support;

FIG. 6 presents data on the changes ("C (%)") in pressure drop ("% DP") and tube packing density ("% TPD") resulting from the use of various sizes (outer diameters) of hollow cylinder support material with different length-to-diameter ratios ("L/D") in a 21 mm diameter reactor tube relative to the use of a standard 6 mm hollow cylinder support material; and

FIG. 7 depicts drawings of the cross-sections of the outside perimeters of (a) the shaped support material being an ideal cylinder, and (b) a cross-section of the shaped support material being a deviation from an ideal cylinder.

One method of manufacturing ethylene oxide is by the catalyzed partial oxidation of ethylene with oxygen. The process is described in general in Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 9, pages 432 to 471, John Wiley, London/New York 1980. Conventional ethylene oxidation reactor systems are suitable for use in the present invention, and they include a plurality of parallel elongated tubes that have inside diameters in the range of from 20 mm to 60 mm and lengths in the range of from 3 m to 15 m. Larger tubes for use in ethylene oxidation reactor system may also be possible. The tubes are typically suitable for use

in a shell-and-tube type heat exchangers and are formed into a bundle for placement into the shell of the heat exchanger. The tubes are packed with any suitable ethylene oxidation catalyst that provides for the partial oxidation of ethylene with oxygen to ethylene oxide. The shell side of the heat exchanger provides for the passage of a heat transfer medium for the removal of the heat of reaction resulting from the oxidation of ethylene and for the control of the reaction temperature within the tubes containing the ethylene oxidation catalyst.

A feedstream comprising ethylene and oxygen is introduced into the tubes of the reactor system wherein the feedstream is contacted with the ethylene oxidation catalyst, typically at temperature in the range of from 50°C to 400°C, and typically under a pressure in the range of from 0.15 MPa to 3 MPa.

The catalyst system used in the typical ethylene oxide manufacturing processes described above are supported catalyst systems that include a support or carrier material upon which is deposited or into which is impregnated a catalytic component and, if desired, a catalyst promoter component or components.

The inventive reactor system can be used in the oxidation of ethylene to ethylene oxide and includes a combination of a reactor tube and a shaped support material that is preferably a catalyst system. The unique geometry of this combination provides various unexpected process benefits.

The catalyst system component of the inventive reactor system can include a shaped support material that supports a catalytic component. Optionally, the shaped support material also supports one or more catalyst promoter components or catalyst copromoter components. The preferred catalytic component is silver. As for the promoter component, it can

include, for example, rare earth metals, magnesium, rhenium, and alkali metals, such as lithium, sodium, potassium, rubidium and cesium. Among these, rhenium and the alkali metals, in particular, the higher alkali metals, such as, lithium, potassium, rubidium and cesium, are preferred. Most preferred among the higher alkali metals is cesium. Either the rhenium promoter may be used without an alkali metal promoter being present or an alkali metal promoter may be used without a rhenium promoter being present or a rhenium promoter and an alkali metal promoter can both be present in the catalyst system. In addition to the aforementioned promoters, a rhenium copromoter can be present in the catalyst system. Such copromoters can include sulfur, molybdenum, tungsten, and chromium. The promoter and copromoter compounds can be applied to the support material by any suitable method, for example by impregnation, and in any form.

The support material of the shaped support material and of the catalyst system can be any commercially available heat-resistant and porous material suitable for use as support material for the silver catalyst and promoter components of the catalyst system. The support materials should be relatively inert under the reaction conditions prevailing in the oxidation of ethylene, and in the presence of the chemical compounds used. The support material can include carbon, carborundum, silicon carbide, silicon dioxide, aluminum oxide and mixtures based on aluminum oxide and silicon dioxide. α -alumina is preferred, since it has a largely uniform pore diameter. The support material has typically a specific surface area of 0.1 to 10 m²/g, preferably 0.2 to 5 m²/g and more preferably from 0.3 to 3 m²/g (measured by the well-known B.E.T. method, see Brunauer, Emmet and Teller in *J. Am. Chem. Soc.* 60 (1938) 309-316, which is incorporated herein by reference); typically a

specific pore volume of from 0.1 to 1.5 cm³/g, preferably from 0.2 to 1.0 cm³/g and most preferably from 0.3 to 0.8 cm³/g (measured by the well-known water adsorption method, that is ASTM C20); typically an apparent porosity of 20 to 120% by volume, preferably 40 to 80% by volume (measured by the water adsorption method); typically a mean pore diameter of 0.3 to 15 μm, preferably 1 to 10 μm; and typically a percentage of pores having a diameter of 0.03 to 10 μm of at least 50% by weight (measured by mercury intrusion to a pressure of 3.0 x 10⁸ Pa using a Micromeritics Autopore 9200 model (130° contact angle, mercury with a surface tension of 0.473 N/m, and correction for mercury compression applied).

The silver catalyst component and promoter components of the catalyst system are deposited on or impregnated into the support material of the catalyst system by any standard method known in the art. The catalyst system should typically have a concentration of silver or silver metal in the range of from 2 weight percent to 30 weight percent, or even higher, for example up to 40 weight percent, or up to 50 weight percent, with the weight percent being based on the total weight of the catalyst system including the weight of the support material, the weight of the catalyst component, i.e., silver metal, and the weight of the promoter component or components. In some embodiments, it is preferred for the silver component of the catalyst system to be present at a concentration in the range of from 4 weight percent to 22 weight percent and, most preferably, from 6 to 20 weight percent. In other embodiments, it is preferred for the silver component of the catalyst system to be present at a concentration in the range of from more than 20 to less than 30 weight percent and, more preferably, from 22 to 28 weight percent. The promoter or promoters can be present in the

catalyst system at a concentration in the range of from 0.003 weight percent to 1.0 weight percent, preferably from 0.005 to 0.5 weight percent and, most preferably, from 0.01 to 0.2 weight percent.

The inventive reactor system provides for an improved balance of the tube packing density (TPD), also the bed voidage and the catalyst hold-up, relative to the pressure drop across the packed bed when in use in an ethylene oxide manufacturing process, as compared to conventional systems. An important aspect of this invention is the recognition that such an improvement can be obtained, for example, by changing the ratio of the nominal outside diameter to the nominal inside diameter of the hollow cylinder geometric configuration. This is truly unexpected because catalysts based on hollow cylinder support materials have been employed in processes for the manufacture of ethylene oxide already for many years and much effort has been devoted to improving the performance of such catalyst. However, attempts to improve the performance of these catalysts by modifying the geometry of the hollow cylinder geometric configuration do not seem to have received attention.

In accordance with this invention, the improved balance is obtained, for example, by changing, typically increasing, the ratio of the nominal outside diameter to the nominal inside diameter of the hollow cylinder geometric configuration, compared to the ratio of conventional hollow cylinder support material. The improved balance may be found by comparative testing, as described hereinbefore, using a hollow cylinder support material versus a standard hollow cylinder support material having the employed dimensions as conventionally employed. In this comparative testing the materials typically have the same material density. Otherwise, a difference in material densities is corrected

for, so that changes in the tube packing density reflect truly changes in the catalyst hold-up and the bed voidage. A positive test result, as defined hereinbefore, is indicative of an improved balance. Examples of the comparative testing have been provided in Examples I-IV, hereinafter.

An improved balance of the tube packing density (TPD) relative to the pressure drop across the packed bed may come in various appearances or qualities, as will be apparent from the description hereinafter.

The inventive reactor system includes a packed bed of the shaped support material or catalyst system having a greater tube packing density than is found in conventional reactor systems. In many instances, it is desirable to increase the tube packing density because of the resulting benefits in catalyst performance. However, it is generally expected that to obtain higher tube packing densities, the pressure drop across the packed bed when in use will increase relative to standard reactor systems. The inventive reactor system, on the other hand, unexpectedly provides for less of an incremental increase in the pressure drop across the packed bed contained within the reactor tube of the reactor system than is expected, and, in many cases, a decrease in pressure drop across the packed bed, when compared to conventional systems, without a corresponding loss in tube packing density and, in many instances, with an increase in tube packing density.

It is preferred for the inventive reactor system to include a packed bed having a tube packing density at least as great as is found in conventional reactor systems, but preferably exceeding the tube packing densities seen in conventional systems, that when in use exhibit pressure drops that decrease with the aforementioned increase in tube packing density.

The relative geometries between the tube diameter and the shaped supports and/or catalyst systems is an important feature of the inventive reactor system, which includes the combination of a reactor tube packed with a bed of shaped supports which preferably include catalytic components to provide the catalyst systems. It is also unexpected that larger supports, relative to the reactor tube, can be loaded as a packed bed within the reactor tube to obtain an increase in tube packing density either without observing a larger pressure drop across the packed bed when the reactor system is in use or with observing an incremental increase in pressure drop that is less than expected, particularly based on certain engineering correlations, for example the Ergun Correlation, see W.J. Beek and K.M.K. Muttzall, "Transport Phenomena", J. Wiley and Sons Ltd, 1975, p. 114.

Larger supports and catalyst systems are particularly desired for use in the packed bed of the inventive reactor system with the packed bed having a greater tube packing density than is expected for the particular size of the support or catalyst system but which provides for no incremental pressure drop increase when in use and, preferably, an incremental decrease in pressure drop relative to that which is expected for reactor systems with the same tube packing density. An additional benefit can be an increase in the tube packing density.

In order to obtain the aforescribed benefits, the inventive reactor system should include certain geometries. It has also been determined that these geometries are influenced by reactor tube diameters and, thus, the relative geometries of the reactor tube and the shaped supports are typically different for different tube diameters. For reactor tubes having an internal diameter of less than 28 mm, the ratio of the reactor tube internal diameter and support

system outside diameter should be in the range of from 1.5 to 7, preferably, from 2 to 6 and, most preferably, from 2.5 to 5. For reactor tubes having an internal diameter exceeding 28 mm, the ratio of reactor tube internal diameter and catalyst support outside diameter should be in the range of from 2 to 10, preferably, from 2.5 to 7.5 and, most preferably, from 3 to 5.

The ratio of outside diameter to bore or inside diameter of the support of the catalyst system is another important feature of the inventive reactor system. For reactor tubes having an internal diameter of less than 28 mm, the ratio of outside diameter to bore or inside diameter of the support of the catalyst system can be in the range of from 2.3 to 1000, preferably, from 2.6 to 500 and, most preferably, from 2.9 to 200. For reactor tubes having an internal diameter exceeding 28 mm, the ratio of outside diameter to bore or inside diameter of the support of the catalyst system can be in the range of from 2.7 to 1000, preferably, from 3 to 500 and, most preferably, from 3.3 to 250.

While it is important for the bore diameter of the shaped support material to be relatively small, it is also important for the inside bore of the support to have at least some dimension. It has been found that the void space defined by the bore diameter provides for certain benefits in the manufacturing of the catalyst and its catalytic properties. While not wanting to be bound to any particular theory, it is believed, however, that the void space provided by the bore diameter of the hollow cylinder allows for improved deposition of the catalytic component onto the carrier, for example by impregnation, and improved further handling, such as drying. An advantage of applying a relatively small bore diameter is also that the shaped support material has higher crush strength relative to a

support material having a larger bore diameter. It is preferred to have at at least one end of the bore, typically at both ends, a bore diameter of at least 0.1 mm, more preferably at least 0.2 mm. Preferably the bore diameter is at least 5 mm, and preferably up to 2 mm, for example 1 mm or 1.5 mm.

A further important feature of the inventive reactor system is for the support of the catalyst system of the packed bed of the inventive reactor system to have a length-to-outside diameter ratio in the range of from 0.5 to 2.0, preferably from 0.8 to 1.5 and, most preferably, from 0.9 to 1.1.

A summary of the desired ranges for the geometric dimensions of the inventive reactor system is presented in Tables 1 and 2. Table 1 presents the relative geometries of the shaped supports for reactor tubes having diameters that are less than 28 mm. Table 2 presents the relative geometries of the shaped supports for reactor tubes having diameters that of at least 28 mm. The smaller reactor tubes can have tube diameters that range downwardly to 21 mm or even smaller, for example 20 mm. Thus, the tube diameter of the smaller reactor tubes of the inventive reactor system can be in the range of from 20 mm or 21 mm to less than 28 mm. The larger reactor tubes can have tube diameters that range upwardly to 60 mm or even larger. Thus, the tube diameter of the larger reactor tubes of the inventive reactor system can be in the range of from 28 mm to 60 mm.

For tube diameters in the range of from 28 mm to 60 mm, in particular when the tube diameter is 39 mm, the ratio of the nominal outside diameter to the nominal inside diameter of the of the support is preferably:

at least 4.5, when the outside diameter is in the range of from 10.4 mm to 11.6 mm; or

greater than 3.4, in particular at least 3.6, when the outside diameter is in the range of from 9.4 mm to 10.6 mm;
or

at least 2.6, in particular in the range of from 2.6 to 7.3, when the outside diameter is in the range of from 8.4 mm to 9.6 mm.

Table 1. Inventive Reactor System Geometries For Reactor Tubes
Having Tube Diameters of Less Than 28 mm

	Tube Diameter/Catalyst System Outside Diameter	Catalyst System Length/Catalyst System Outside Diameter	Catalyst Outside Diameter/ Bore Diameter
Broad	1.5 - 7	0.5 - 2	2.3 - 1000
Intermediate	2 - 6	0.8 - 1.5	2.6 - 500
Narrow	2.5 - 5	0.9 - 1.1	2.9 - 200

Table 2. Inventive Reactor System Geometries For Reactor Tubes
Having Tube Diameters of at Least 28 mm

	Tube Diameter/Catalyst System Outside Diameter	Catalyst System Length/Catalyst System Outside Diameter	Catalyst Outside Diameter/ Bore Diameter
Broad	2 - 10	0.5 - 2	2.7 - 1000
Intermediate	2.5 - 7.5	0.8 - 1.5	3.0 - 500
Narrow	3 - 5	0.9 - 1.1	3.3 - 250

The reactor tube length can be any length that effectively provides for the proper contact times within the reaction zone between the feed reactants and the catalyst system to give a desired reaction product. Generally, as noted above, the reactor tube length will exceed 3 m and, preferably, it is in the range of from 3 m to 15 m. The full length of the reactor tube can be packed with the catalyst system or any portion of the length of the reactor tube can be packed with the catalyst system to thereby provide a packed bed of the catalyst system having a bed depth. Thus, the bed depth can exceed 3m and, preferably, it is in the range of from 3 meters to 15 meters.

In the normal practice of this invention, a major portion of the packed bed, of the inventive reactor system comprises the shaped support material having the geometries as described herein. Thus, typically, the packed bed of the reactor system will predominately, that is for at least 50 percent, comprise the catalyst system having the specifically defined geometries and, in particular, at least 80 percent of the packed catalyst bed will comprise the specifically defined catalyst system, but, preferably, at least 85 percent and, most preferably, at least 90 percent. When referring to the percent of the packed bed that comprises the catalyst system, it shall mean that the ratio of the total number of individual catalyst system particles having the particular dimensions described herein, to the total number of catalyst system particles contained in the packed bed, multiplied by 100. In another embodiment, when referring to the percent of the packed bed that comprises the catalyst system, it shall mean that the ratio of the bulk volume of the catalyst system particles having the particular dimensions described herein, to the bulk volume of all the catalyst system particles contained in the packed bed, multiplied by 100. In yet

another embodiment, when referring to the percent of the packed bed that comprises the catalyst system, it shall mean that the ratio of the weight of the catalyst system particles having the particular dimensions described herein, to the weight of all the catalyst system particles contained in the packed bed, multiplied by 100.

The tube packing density of the catalyst system bed of the inventive reactor system can be an important feature of the invention; since, catalyst performance improvements can result from the increase in the tube packing density obtainable from using the unique geometries of the inventive reactor system. Generally, the tube packing density of the packed catalyst system bed depends upon the associated reactor tube inside diameter and on the properties, for example, density, of the particular support material used to form the shaped support.

For smaller reactor tube inside diameters the tube packing density of the packed bed can generally be less than the tube packing density of the packed bed of larger reactor tube inside diameters. Thus, for example, the tube packing density of the packed bed of an inventive reactor system having an inside reactor tube diameter of 21 mm can be as low as, but exceeding, 550 kg per cubic meters when the support material is predominantly α -alumina. For reactor tubes having larger inside tube diameters as well as those having smaller diameters, it is desirable to have as great a tube packing density as is achievable and still realize the benefits of the invention. Such a tube packing density when the support material is predominantly α -alumina can exceed 650 kg per cubic meter or can be greater than 700 kg per cubic meter and even greater than 850 kg per cubic meter. Preferably, the tube packing density is greater than 900 kg per cubic meter and, most preferably, the tube packing

density exceeds 920 kg per cubic meter. The tube packing density will generally be less than 1200 kg per cubic meter and, more specifically, less than 1150 kg per cubic meter.

Reference is now made to FIG. 1 which depicts the inventive reactor system 10 comprising an elongated tube 12 and a packed bed 14 contained within elongated tube 12. Elongated tube 12 has a tube wall 16 with an inside tube surface 18 and inside tube diameter 20 that define a reaction zone, wherein is contained packed bed 14, and a reaction zone diameter 20. Elongated tube 12 has a tube length 22 and the packed bed 14 contained within the reaction zone has a bed depth 24. Outside the bed depth 24, the elongated tube 12 may contain a separate bed of particles of a non-catalytic material for the purpose of, for example, heat exchange with a feedstock and/or another such separate bed for the purpose of, for example, heat exchange with a reaction product. The elongated tube 12 further has an inlet tube end 26 into which a feedstock comprising ethylene and oxygen can be introduced and an outlet tube end 28 from which a reaction product comprising ethylene oxide and ethylene can be withdrawn. It is noted that the ethylene in the reaction product, if any, is the ethylene of the feedstock which passes through the reactor zone unconverted. Typical conversions of the ethylene exceed 10 mole percent, but, in some instances, the conversion may be less.

The packed bed 14 contained within the reaction zone is composed of a bed of supported catalyst system 30 as depicted in FIG. 2. The supported catalyst system 30 has a generally hollow cylinder geometric configuration with a nominal length 32, nominal outside diameter 34, and nominal inside or bore diameter 36, in accordance with this invention.

The skilled person will appreciate that the expression "cylinder" does not necessarily mean that the hollow cylinder

geometric configuration comprises an exact cylinder. The expression "cylinder" is meant to include insignificant deviations from an exact cylinder. For example, the cross-section of the outer perimeter of the hollow cylinder geometric configuration perpendicular to the cylinder axis is not necessarily an exact circle 71, as depicted in FIG. 7. Also, the axis of the hollow cylinder geometric configuration may be approximately straight and/or the outside diameter of the hollow cylinder geometric configuration may be approximately constant along the axis. Insignificant deviations include, for example, cases where the outside perimeter of the cylinder can be positioned in an imaginary tube-shaped space defined by two imaginary exact coaxial cylinders of virtually the same diameters, whereby the diameter of the imaginary inner cylinder is at least 70%, more typically at least 80%, in particular at least 90%, of the diameter of the imaginary outer cylinder, and the imaginary cylinders are chosen such that the ratio of their diameters is the closest possible to 1. In such cases the diameter of the imaginary outer cylinder is deemed to be the outer diameter of the hollow cylinder geometric configuration. FIG. 7 depicts in a cross-sectional view, taken perpendicular to the axis of the imaginary cylinders 73 and 74, the outside perimeter 72 of the hollow cylinder geometric configuration, the imaginary outer cylinder 73 and the imaginary inner cylinder 74.

Similarly, the skilled person will appreciate that the bore of the hollow cylinder geometric configuration may not be necessarily exactly cylindrical, the axis of the bore may be approximately straight, the bore diameter may be approximately constant, and/or the axis of the bore may be displaced, or may angle, relative to the axis of the cylinder. If the bore diameter changes over the length of the bore, the bore diameter is deemed to be the largest diameter at a bore end.

If the bore does not is not exactly circular in cross-section, the widest dimension is deemed to be the bore diameter. Also, the void space provided by the bore may be divided over two or more bores, for example 2, 3, or even 4, or 5 bores, in which case the diameters of the bores are such that the total of the cross-sectional areas of the bores is equal to the cross-sectional area of a single bore having a diameter, as specified herein.

In preferred embodiments, the hollow cylinder geometric configuration is intended to be a cylinder having a bore along the axis of the cylinder.

It is understood that the dimensions of the hollow cylinder geometric configuration are nominal and approximate, since, methods of manufacturing the shaped agglomerates are not necessarily precise.

It is the unique geometric combination of inside tube diameter or reaction zone diameter 20 and the geometric dimensions of the supported catalyst system 30 that provides for the unexpected reduction in pressure drop, when in use and relative to conventional systems, without a significant decrease in tube packing density. In many instances, and preferably, the tube packing density of the inventive reaction system is greater than that of conventional systems while still providing for a reduction in pressure drop when in use.

An essential geometric dimension of the catalyst system 30 is the ratio of nominal length 32 to nominal outside diameter 34. This dimension is described in detail above.

Another essential geometric dimension of the catalyst system 30 is the ratio of the nominal outside diameter 34 to nominal inside diameter 36. This dimension is described in detail above.

The relative dimensions between the catalyst system 30 and elongated tube 12 are an important aspect of the invention; since, these dimensions determine the tube packing density and pressure drop characteristics associated with reactor system 10. This dimension is described in detail above.

Another way of defining the catalyst system is by reference to its nominal dimensions. For a standard 8 mm catalyst having a hollow cylinder geometric configuration, the outer diameter of the cylinder is nominally 8 mm but can be in the range from 7.4 mm to 8.6 mm. The length of the cylinder is nominally 8 mm but can be in the range from 7.4 mm to 8.6 mm. For use in this invention, the bore diameter can be at least 0.1 mm or 0.2 mm, and preferably in the range of from 0.5 mm to 3.5 mm, more preferably from 0.5 mm to less than 3 mm.

For a standard 9 mm catalyst having a hollow cylinder geometric configuration, the outer diameter of the cylinder is normally 9 mm but can be in the range of from 8.4 mm to 9.6 mm. The cylinder length while nominally 9 mm can be in the range of from 8.4 mm to 9.6 mm. For use in this invention, the bore diameter of the standard 9 mm catalyst can be at least 0.1 mm or 0.2 mm, and preferably in the range of from 0.5 mm to 3.5 mm, more preferably from 1.25 mm to 3.5 mm.

For a standard 10 mm catalyst having a hollow cylinder geometric configuration, the outer diameter of the cylinder is normally 10 mm but can be in the range of from 9.4 mm to 10.6 mm. The cylinder length while nominally 10 mm can be in the range of from 9.4 mm to 10.6 mm. For use in this invention, the bore diameter of the standard 10 mm catalyst can be at least 0.1 mm or 0.2 mm, and preferably in the range

of from 0.5 mm to 4.0 mm, more preferably from 0.5 mm to 3 mm, even more preferably from 0.5 mm to 2.8 mm.

For a standard 11 mm catalyst having a hollow cylinder geometric configuration the outer diameter of the cylinder is normally 11 mm but can be in the range of from 10.4 mm to 11.6 mm. The cylinder length while nominally 11 mm can be in the range of from 10.4 mm to 11.6 mm. For use in this invention, the bore diameter of the standard 11 mm catalyst can be at least 0.1 mm or 0.2 mm, and preferably in the range of from 0.5 mm to 3.5 mm, more preferably from 0.5 mm to 2.5 mm.

Much of the variance in the catalyst system dimensions is due to the manner by which the hollow cylinder support material is manufactured. The manufacturing methods are known in the art of catalyst support manufacture and include such standard methods as extrusion methods and pill manufacturing methods.

FIG. 3 is a schematic representation showing generally an ethylene oxide manufacturing process 40 with a shell-and-tube heat exchanger 42 which is equipped with a plurality of reactor systems as depicted in FIG. 1. Typically the reactor system of FIG. 1 is grouped together with a plurality of other reactor systems into a tube bundle for insertion into the shell of a shell-and-tube heat exchanger.

A feedstock comprising ethylene and oxygen is charged via conduit 44 to the tube side of shell-and-tube heat exchanger 42 wherein it is contacted with the catalyst system contained therein. The heat of reaction is removed by use of a heat transfer fluid such as oil, kerosene or water which is charged to the shell side of shell-and-tube heat exchanger 42 by way of conduit 46 and the heat transfer fluid is removed from the shell of shell-and-tube heat exchanger 42 through conduit 48.

The reaction product comprising ethylene oxide, unreacted ethylene, unreacted oxygen and, optionally, other reaction products such as carbon dioxide and water, is withdrawn from the reactor system tubes of shell-and-tube heat exchanger 42 through conduit 50 and passes to separation system 52. Separation system 52 provides for the separation of ethylene oxide and ethylene and, if present, carbon dioxide and water. An extraction fluid such as water can be used to separate these components and is introduced to separation system 52 by way of conduit 54. The enriched extraction fluid containing ethylene oxide passes from separation system 52 through conduit 56 while unreacted ethylene and carbon dioxide, if present, passes from separation system 52 through conduit 58. Separated carbon dioxide passes from separation system 52 through conduit 61. A portion of the gas stream passing through conduit 58 can be removed as a purge stream through conduit 60. The remaining gas stream passes through conduit 62 to recycle compressor 64. A feedstream containing ethylene and oxygen passes through conduit 66 and is combined with the recycle ethylene that is passed through conduit 62 and the combined stream is passed to recycle compressor 64. Recycle compressor 64 discharges into conduit 44 whereby the discharge stream is charged to the inlet of the tube side of the shell-and-tube heat exchanger 42. Advantageously, separation system 52 is operated in such a way that the quantity of carbon dioxide in the feedstream through conduit 44 is low, for example, below 2 mole-%, preferably below 1 mole-%, or in the range of from 0.5 to 1 mole-%.

The ethylene oxide produced in the epoxidation process may be converted into ethylene glycol, an ethylene glycol ether or an alkanolamine.

The conversion into the ethylene glycol or the ethylene glycol ether may comprise, for example, reacting the ethylene oxide with water, suitably using an acidic or a basic catalyst. For example, for making predominantly the ethylene glycol and less ethylene glycol ether, the ethylene oxide may be reacted with a ten fold molar excess of water, in a liquid phase reaction in presence of an acid catalyst, e.g. 0.5-1.0 %w sulfuric acid, based on the total reaction mixture, at 50-70 °C at 100 kPa absolute, or in a gas phase reaction at 130-240 °C and 2000-4000 kPa absolute, preferably in the absence of a catalyst. If the proportion of water is lowered the proportion of ethylene glycol ethers in the reaction mixture is increased. The ethylene glycol ethers thus produced may be a di-ether, tri-ether, tetra-ether or a subsequent ether. Alternative ethylene glycol ethers may be prepared by converting the ethylene oxide with an alcohol, in particular a primary alcohol, such as methanol or ethanol, by replacing at least a portion of the water by the alcohol.

The conversion into the alkanolamine may comprise reacting ethylene oxide with an amine, such as ammonia, an alkyl amine or a dialkylamine. Anhydrous or aqueous ammonia may be used. Anhydrous ammonia is typically used to favor the production of monoalkanolamine. For methods applicable in the conversion of ethylene oxide into the alkanolamine, reference may be made to, for example US-A-4845296, which is incorporated herein by reference.

Ethylene glycol and ethylene glycol ethers may be used in a large variety of industrial applications, for example in the fields of food, beverages, tobacco, cosmetics, thermoplastic polymers, curable resin systems, detergents, heat transfer systems, etc. Alkanolamines may be used, for example, in the treating ("sweetening") of natural gas.

The following examples are intended to illustrate the advantages of the present invention and are not intended to unduly limit the scope of the invention.

Example I

This Example I presents the testing procedure used to evaluate the pressure drop and tube packing density characteristics of the inventive reactor system relative to a standard reactor system.

Various hollow cylinder carriers having different sizes and geometries were tested in a commercial length reactor tube of either a 39 mm internal diameter or a 21 mm internal diameter. The reactor tubes were set up to measure differential pressure drop across the carrier bed. Tube packing density of the carrier bed was determined.

The particular carrier to be tested was loaded into the reactor tube using a standard funnel loading process. The carrier was weighed to determine its mass prior to being charged to the reactor tube. After the reactor tube was charged with the carrier, a 0.79 MPa (100 psig) air source was used to perform a 15 second dust blow down. The carrier bed height was measured.

The tube packing density was determined by using the mass of carrier loaded into the reactor tube, the measured height of the carrier bed, and the internal diameter of the reactor tube. The tube packing density has units of mass per volume and is defined by the following formula:

$$4m/\pi d^2 h$$

where: m is the mass of the carrier loaded into the reactor tube,
 d is the diameter of the reactor tube, and
 h is the height of the carrier bed contained within the reactor tube.

After the reactor tube was loaded with the carrier, it was sealed and pressure tested at 1.342 MPa (180 psig). The reactor tube was equipped with an inlet and an outlet. Nitrogen gas was introduced into the inlet of the packed reactor tube at a pressure of about 1.136 MPa (150 psig). For each of about 11 different nitrogen gas flow rates in a turbulent flow regime (Reynolds particle number in excess of 700, see W.J. Beek and K.M.K. Muttzall, "Transport Phenomena", J. Wiley and Sons Ltd, 1975, p. 114) a differential pressure drop (pressure drop) across the carrier bed of the reactor tube was determined by measuring the tube inlet pressure and the tube outlet pressure. The inlet and outlet temperatures of the nitrogen gas were also measured. The pressure drop was evaluated per unit length of packed bed. The tube packing densities were corrected for small differences in the intrinsic material densities of the different carriers, in order to reflect differences in the catalyst hold-up caused by the differences in carrier geometries.

Example II

This Example II presents a summary of the results from using the testing procedure described in Example I for hollow cylinder carriers of nominal sizes 5 mm, 6 mm, 7 mm, 8 mm and 9 mm having a nominal length-to-diameter (L/D) ratio of either 0.5 or 1.0 packed into a 39 mm reactor tube. The following are the particulars of the carrier dimensions:

9 mm: L/D = 1.0, bore diameter 3.85 mm

9 mm: L/D = 0.5, bore diameter 3.90 mm

8 mm: L/D = 1.0, bore diameter 3.20 mm ("standard 8 mm")

8 mm: L/D = 0.5, bore diameter 3.30 mm

7 mm: L/D = 1.0, bore diameter 2.74 mm

7 mm: L/D = 0.5, bore diameter 2.75 mm

6 mm: $L/D = 1.0$, bore diameter 2.60 mm ("standard 6 mm")
6 mm: $L/D = 0.5$, bore diameter 2.60 mm
5 mm: $L/D = 1.0$, bore diameter 2.40 mm
5 mm: $L/D = 0.5$, bore diameter 2.70 mm

Summary data for the percent changes in pressure drop across the carrier bed and the percent changes in tube packing density relative to the standard 8 mm carrier are presented in FIG. 4. As is shown, for carrier sizes smaller than 8 mm and for all carrier sizes having an L/D ratio of 0.5, the pressure drop across the carrier bed increases. The data presented in FIG. 4 does show, however, that in a 39 mm reactor tube, the larger 9 mm carrier that has an L/D ratio of 1.0 provides an improved pressure drop relative to the standard 8 mm carrier.

Example III

This Example III presents the results from using the testing procedure described in Example I for cylinder carriers of nominal sizes 9 mm, 10 mm, and 11 mm with a nominal L/D ratio of 1.0 into a 39 mm reactor tube. Some of the carriers were solid cylinders, other carriers were hollow cylinders with different bore diameters, as specified in FIG. 5. Summary data for the percent changes in pressure drop across the carrier bed and the percent changes in tube packing density relative to the standard 8 mm carrier are presented in FIG. 5.

The data presented in FIG. 5 show an unexpected reduction in pressure drop that results from using the unique combination of reactor tube and support geometry. For the 9 mm carrier having a ratio of bore diameter -to outside diameter greater than 0.138 (ratio of outside diameter to bore diameter less than 7.2) there is an improvement in pressure drop, relative to the standard 8 mm carrier tested,

and for all the tested 10 mm and 11 mm carrier geometries there is an improvement in pressure drop, relative to the standard 8 mm carrier.

As for the tube packing densities, an improvement is seen in the 9 mm carrier tube packing densities, relative to the standard 8 mm carrier, for geometries in which the ratio of bore diameter to outside diameter is equal or less than about 0.38 (ratio of outside diameter to bore diameter at least 2.6) and, for the 10 mm carrier, an improvement is seen for the geometries having a ratio of bore diameter to outside diameter of equal or less than about 0.28 (ratio of outside diameter to bore diameter greater than 3.4, preferably at least 3.6). For the 11 mm carrier, improvements are seen in both the pressure drop and tube packing density for all the geometries tested, that is at a ratio of outside diameter to bore diameter of greater than 4.5.

Example IV

This Example IV presents the results from using the testing procedure described in Example I for nominal carrier sizes 5 mm, 6 mm, 7 mm, 8 mm and 9 mm having a nominal L/D ratio of either 0.5 or 1.0 packed into a 21 mm reactor tube. The particulars of the carrier dimensions have been specified in Example II.

Summary data for the percent changes in pressure drop across the carrier bed and the percent changes in tube packing density relative to the standard 6 mm carrier are presented in FIG. 6. As is shown, for the 8 mm and 9 mm carrier sizes an improvement in pressure drop is observed and for the 7 mm carrier having an L/D of 1.0 an improvement in pressure drop is observed. With selected carriers, an improvement in pressure drop can be achieved, without decreasing the tube packing density, in particular when increasing the ratio of outside diameter to bore diameter.

Example V (hypothetical)

Each of the carriers described in Examples II-IV is impregnated with a solution comprising silver, to form a silver catalyst comprising the carrier. A feed stream comprising ethylene and oxygen is then contacted with the catalyst at suitable conditions to form ethylene oxide.

Example VI

This Example VI presents information concerning the properties and geometric configuration of the two types of carriers (i.e., Carrier C, and Carrier D) used in the preparation of the catalysts as described in Example VII, (cf. Table 3).

Table 3. Properties of Carriers

	Carrier C	Carrier D
<u>Properties</u>		
Water Absorption, %	46.5	50.4
Bulk Packing Density, kg/m ³ (lbs/ft ³)	843 (52.7)	788 (49.2)
ASTM Attrition Loss, %	14.7	16.5
Average Flat Plate Crush Strength, N (lbf)	130 (29.3)	180 (40.4)
Surface Area, m ² /g	0.77	0.78
<u>Geometric Configuration</u>		
Nominal Size, mm	8	8
Average Length, mm	7.7	7.7
Length, Range, mm	6.6-8.6	6.6-8.6
Diameter, mm	8.6	8.6
Bore Diameter, mm	1.02	1.02
Ratio Length/Outside Diameter	0.90	0.90

Example VII

This Example VII describes the preparation of catalysts which can be employed in the present invention.

Catalyst C:

Catalyst C prepared by impregnation of Carrier C using the methods known from US-A-4766105, which US patent is incorporated herein by reference. The final Catalyst C composition was 17.8% Ag, 460 ppm Cs/g catalyst, 1.5 μ mole Re/g catalyst, 0.75 μ mole W/g catalyst, and 15 μ mole Li/g catalyst.

Catalyst D:

Catalyst D was prepared in two impregnation steps. In the first impregnation the carrier was impregnated with a silver solution, according to the procedure for catalyst C, except that no dopants were added to the silver solution. After drying, the resulting dried catalyst precursor contained approximately 17 wt% silver. The dried catalyst precursor was then impregnated with a solution which contained silver and the dopants. The final Catalyst D composition was 27.3% Ag, 550 ppm Cs/g catalyst, 2.4 μ mole Re/g catalyst, 0.60 μ mole W/g catalyst, and 12 μ mole Li/g catalyst.

Catalyst E:

Catalyst E was prepared in two impregnation steps, according to the procedure applied for Catalyst D, except that the tungsten compound was present in the first impregnation solution instead of the second impregnation solution. The final Catalyst E composition was 27.3% Ag, 560 ppm Cs/g catalyst, 2.4 μ mole Re/g catalyst, 0.60 μ mole W/g catalyst, and 12 μ mole Li/g catalyst.

While this invention has been described in terms of the presently preferred embodiment, reasonable variations and modifications are possible by those skilled in the art. Such variations and modifications are within the scope of the described invention and the appended claim.

C L A I M S

1. A reactor system comprising:

an elongated tube having a tube length and a tube diameter which define a reaction zone; wherein contained within the reaction zone is a packed bed of shaped support material; and wherein the shaped support material has a hollow cylinder geometric configuration defined by a nominal length, a nominal outside diameter and a nominal inside diameter such that the ratio of the nominal length to the nominal outside diameter is in the range of from 0.5 to 2, and further such that,

when the tube diameter is less than 28 mm, the ratio of the nominal outside diameter to the nominal inside diameter exceeds 2.3, and the ratio of the tube diameter to the outside diameter is in the range of from 1.5 to 7, and,

when the tube diameter is at least 28 mm, the ratio of the nominal outside diameter to the nominal inside diameter exceeds 2.7, and the ratio of the tube diameter to the outside diameter is in the range of from 2 to 10.

2. A reactor system comprising:

an elongated tube having a tube length and a tube diameter which define a reaction zone; wherein contained within the reaction zone is a packed bed of shaped support material; and wherein the shaped support material has a hollow cylinder geometric configuration defined by a nominal length, a nominal outside diameter and a nominal inside diameter such that

the ratio of the nominal length to the nominal outside diameter is in the range of from 0.5 to 2, and

the ratio of the nominal outside diameter to the nominal inside diameter provides a positive test result, and further such that

the ratio of the tube diameter to the nominal outside diameter is in the range of from 1.5 to 7, when the tube diameter is less than 28 mm, and in the range of from 2 to 10, when the tube diameter is at least 28 mm;

wherein "positive test result" is defined by a decrease of the quotient of a numerical value of the pressure drop per unit length of the packed bed and a numerical value of the packing density, which numerical values are obtained by testing the packed bed in a turbulent flow of nitrogen gas at a pressure of 1.136 MPa (150 psig), relative to a comparison quotient of numerical values obtained in an identical manner, except that the hollow cylinder geometric configuration of the same support material is defined by

a nominal outside diameter of 6 mm and a nominal inside diameter of 2.6 mm, when the tube diameter is less than 28 mm, and a nominal outside diameter of 8 mm and a nominal inside diameter of 3.2 mm, when the tube diameter is at least 28 mm, and

a ratio of the nominal length to the nominal outside diameter of 1.

3. A reactor system as claimed in claim 2, wherein the hollow cylinder geometric configuration is defined such that,

when the tube diameter is less than 28 mm, the ratio of the nominal outside diameter to the nominal inside diameter exceeds 2.3, and,

when the tube diameter is at least 28 mm, the ratio of the nominal outside diameter to the nominal inside diameter exceeds 2.7.

4. A reactor system as claimed in any of claims 1-3, wherein the tube diameter is in the range of from 28 mm to 60 mm, and

the ratio of the nominal outside diameter to the nominal inside diameter is

at least 4.5, when the outside diameter is in the range of from 10.4 mm to 11.6 mm; or

greater than 3.4, when the outside diameter is in the range of from 9.4 mm to 10.6 mm; or

at least 2.6, when the outside diameter is in the range of from 8.4 mm to 9.6 mm.

5. A reactor system as claimed in claim 4, wherein the ratio of the nominal outside diameter to the nominal inside diameter is

at least 4.5, when the outside diameter is in the range of from 10.4 mm to 11.6 mm;

at least 3.6, when the outside diameter is in the range of from 9.4 mm to 10.6 mm; or

in the range of from 2.6 to 7.3, when the outside diameter is in the range of from 8.4 mm to 9.6 mm.

6. A reactor system as claimed in any of claims 1-5, wherein the tube diameter is about 39 mm.

7. A reactor system as claimed in any of claims 1-6, wherein the inside diameter of the hollow cylinder geometric configuration is at least 0.5 mm.

8. A reactor system as claimed in any of claims 1-7, wherein the ratio of nominal outside diameter to nominal inside diameter is in the range of from 2.6 to 500, when the tube diameter is less than 28 mm, and in the range of from 3.0 to 500, when the tube diameter is at least 28 mm.

9. A reactor system as claimed in claim 8, wherein the ratio of nominal outside diameter to nominal inside diameter is in the range of from 2.9 to 200, when the tube diameter is less than 28 mm, and in the range of from 3.3 to 250, when the tube diameter is at least 28 mm.

10. A reactor system as claimed in any of claims 1-9, wherein the tube length is in the range of from 3 to 15 meters.

11. A reactor system as claimed in any of claims 1-10, wherein at 50 percent of the packed bed comprises the shaped support material.
12. A reactor system as claimed in any of claims 1-11, wherein the ratio of the tube diameter to the nominal outside diameter in the range of from 2 to 6, when the tube diameter is less than 28 mm, and in the range of from 2.5 to 7.5, when the tube diameter is at least 28 mm.
13. A reactor system as claimed in claim 12, wherein the ratio of the tube diameter to the nominal outside diameter in the range of from 2.5 to 5, when the tube diameter is less than 28 mm, and in the range of from 3 to 7, when the tube diameter is at least 28 mm.
14. A reactor system as claimed in any of claims 1-13, wherein the shaped support material comprises predominantly alpha-alumina, and the packed bed has a tube packing density greater than 550 kg per cubic meter.
15. A reactor system as claimed in any of claims 1-14, wherein the shaped support material supports a catalytic component.
16. A reactor system as claimed in claim 15, wherein the catalytic component comprises silver.
17. A process for manufacturing ethylene oxide, said process comprises:
 - providing a reactor system as claimed in claim 15 or 16, wherein the elongated tube has an inlet tube end and an outlet tube end;
 - introducing into the inlet tube end a feedstock comprising ethylene and oxygen; and
 - withdrawing from the outlet tube end a reaction product comprising ethylene oxide and unconverted ethylene, if any.
18. A process as claimed in claim 17, wherein the reaction zone is maintained under suitable ethylene oxidative reaction

conditions including a temperature in the range of from 150°C to 400°C and a pressure is in the range of from 0.15 MPa to 3 MPa.

19. A method of using ethylene oxide for making ethylene glycol, an ethylene glycol ether or an 1,2-alkanolamine comprising converting ethylene oxide into ethylene glycol, the ethylene glycol ether, or the 1,2-alkanolamine, wherein the ethylene oxide has been obtained by the process for preparing ethylene oxide as claimed in claim 17 or 18.

20. A catalyst, wherein the catalyst comprises silver supported by a shaped support material which has a hollow cylinder geometric configuration defined by a nominal length, a nominal outside diameter and a nominal inside diameter such that

the ratio of the nominal length to the nominal outside diameter is in the range of from 0.5 to 2,

the ratio of the nominal outside diameter to the nominal inside diameter exceeds 2.7, and

the ratio of the tube diameter to the outside diameter is in the range of from 2 to 10.

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Fig.1.

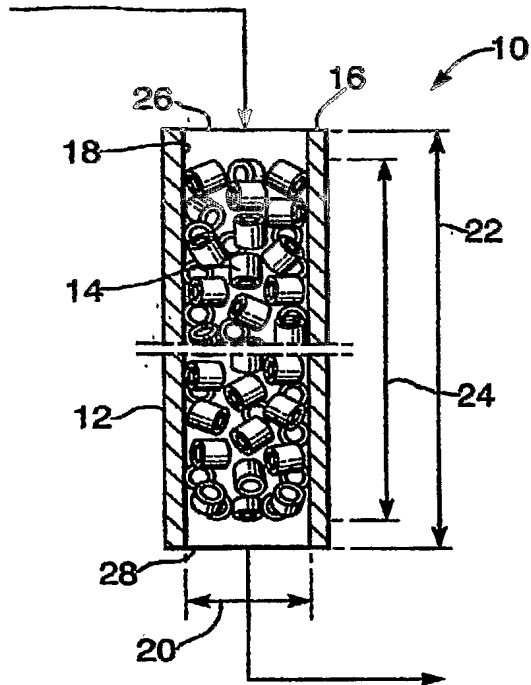


Fig.2.

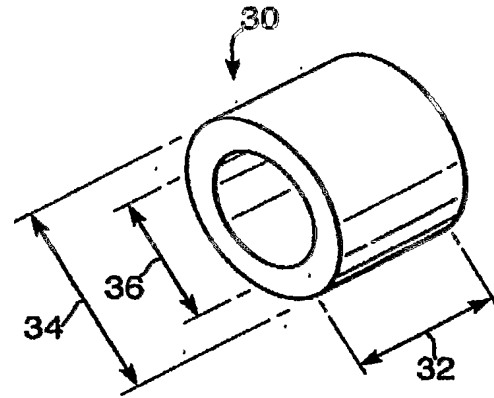
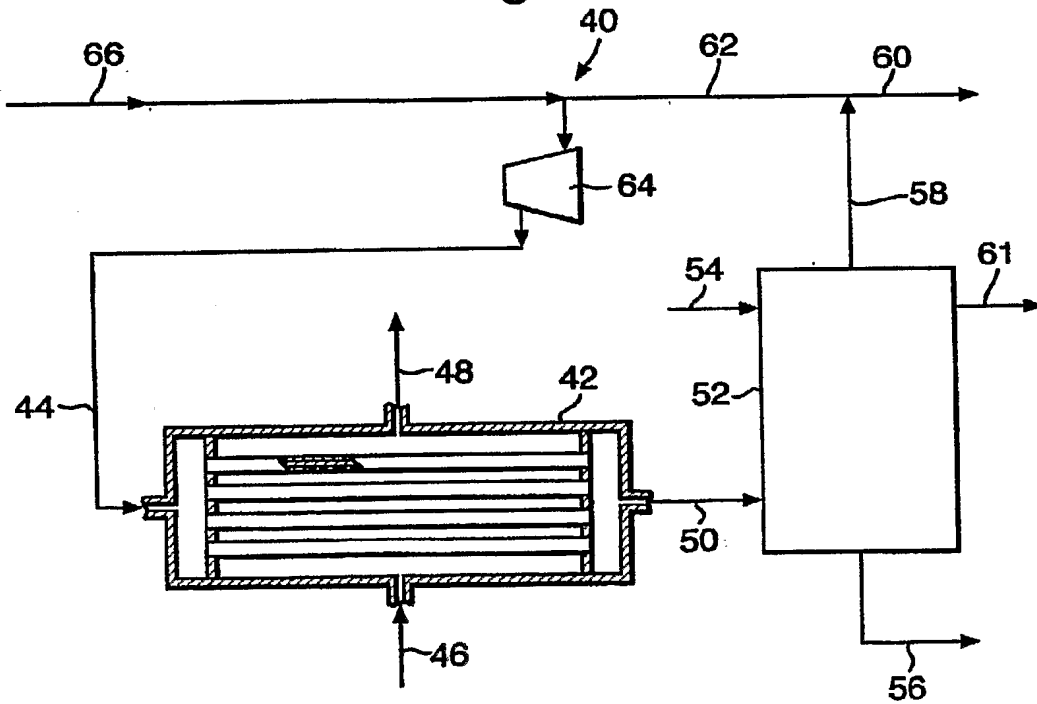
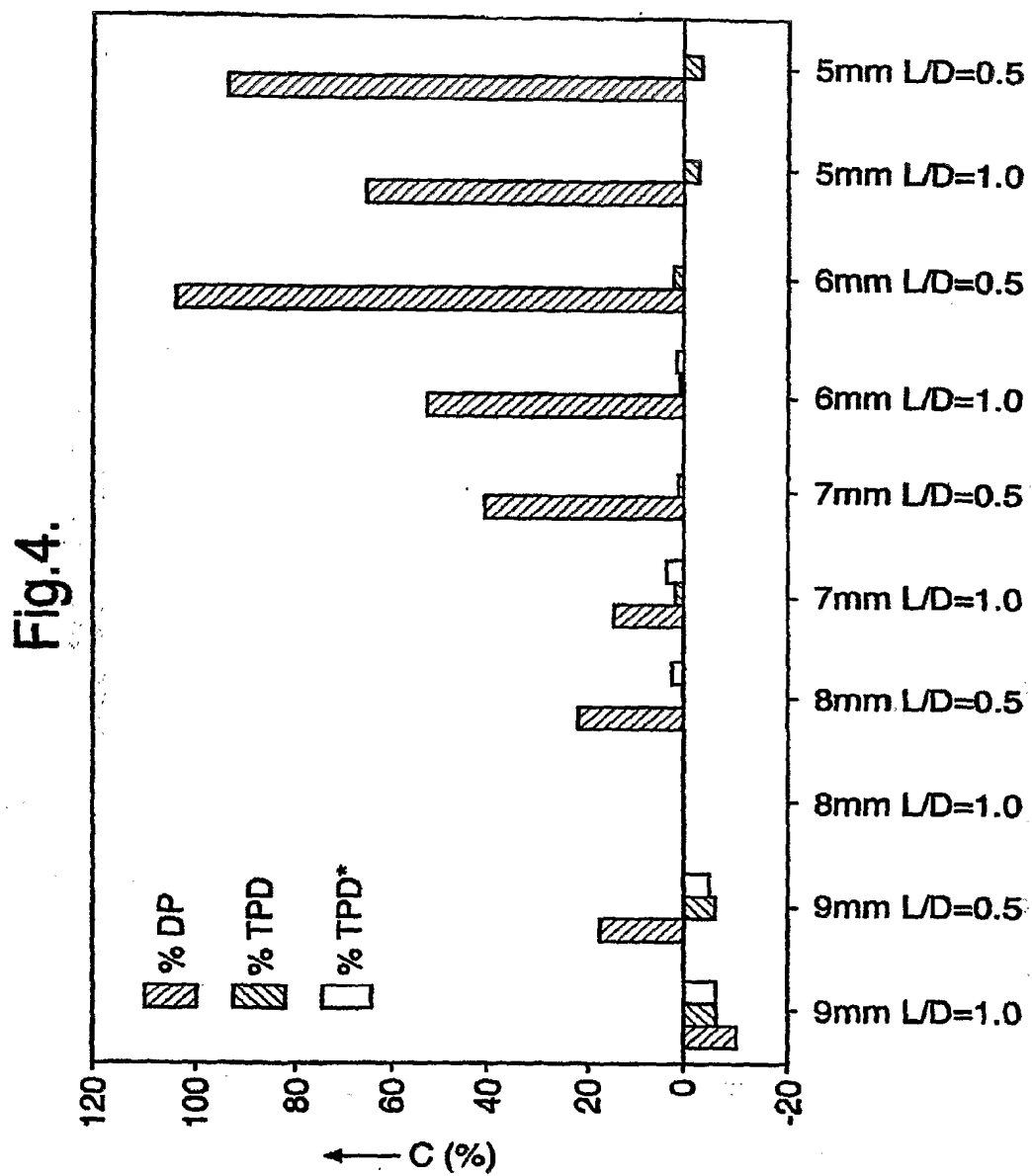


Fig.3.

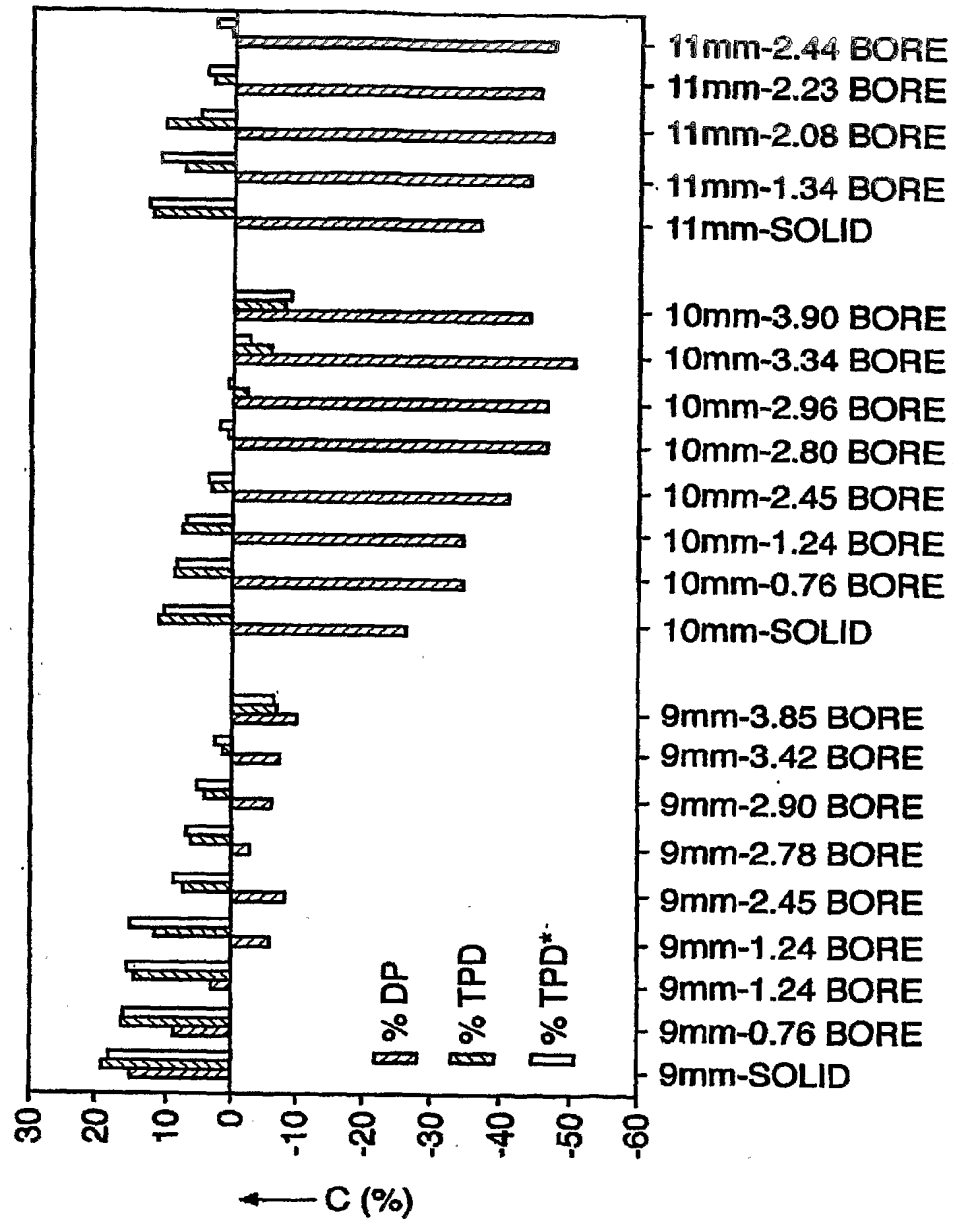


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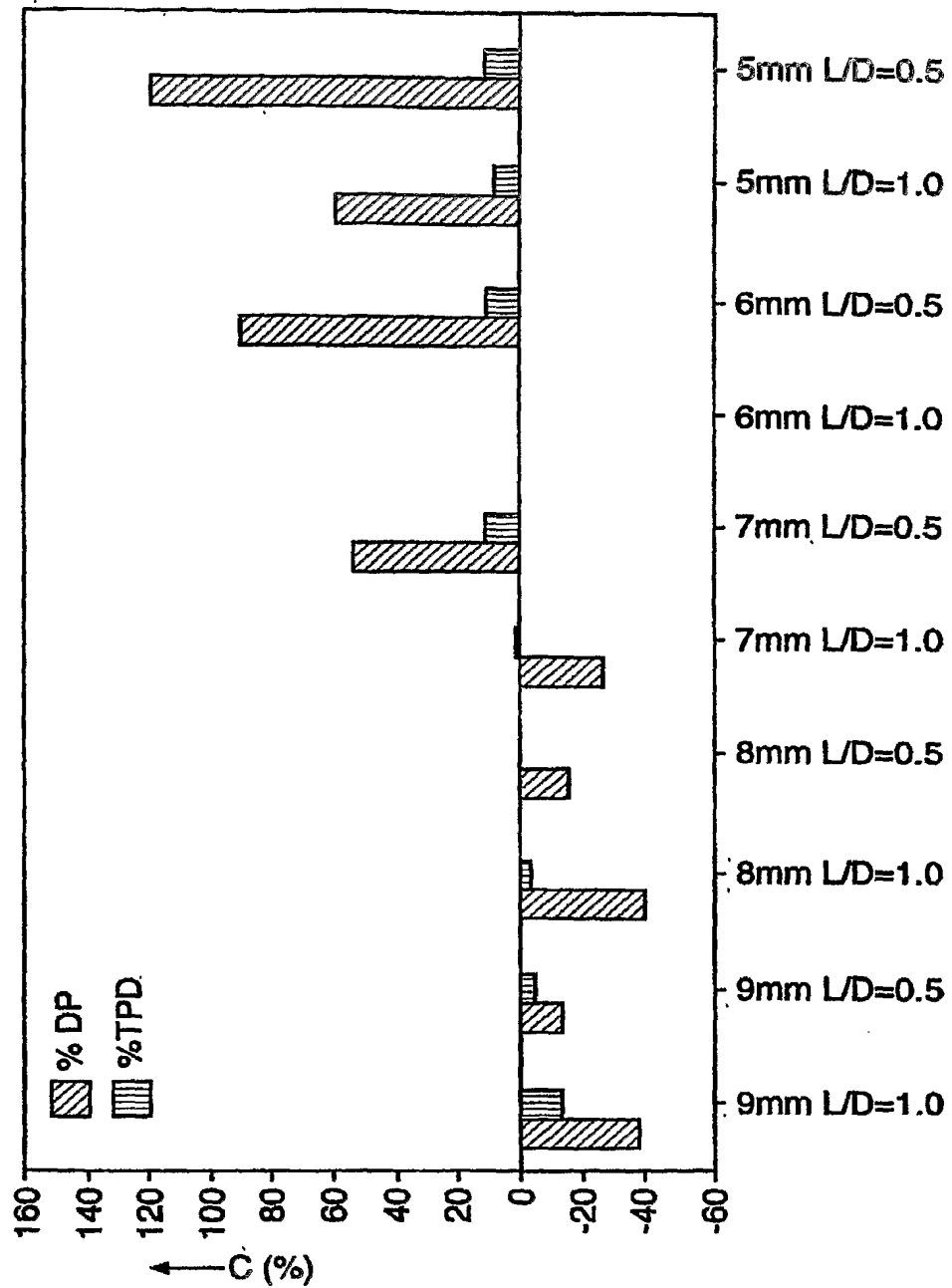
3/5

Fig.5.



4/5

Fig. 6.



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Fig.7a.

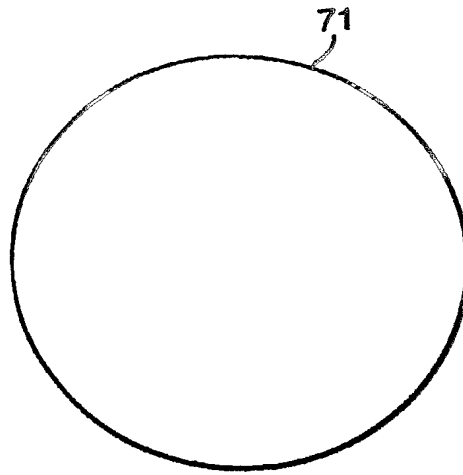
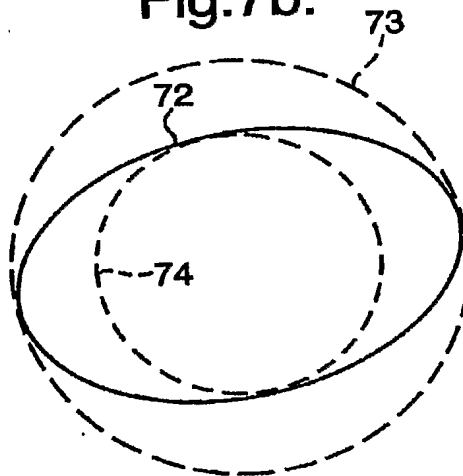


Fig.7b.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/014087

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J19/30 B01J8/06 C07D301/10 B01J35/02 B01J23/50
B01J23/68

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 656 157 A (HOFMANN FRIEDBERT ET AL) 7 April 1987 (1987-04-07) example 1	1,7, 14-16
X	US 4 511 671 A (AOKI RYUJI ET AL) 16 April 1985 (1985-04-16) examples 1,2,4-12	1,7-9, 12,13, 15,16
X	US 4 645 754 A (SAOTOME MINORU ET AL) 24 February 1987 (1987-02-24) column 12, line 24 - line 35	1,7, 10-12, 14,15, 17-19
X	EP 1 277 698 A (KELLOGG BROWN & ROOT INC) 22 January 2003 (2003-01-22) the whole document	1
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

13 September 2004

Date of mailing of the international search report

23/09/2004

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/014087

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/010378 A1 (KAKIMOTO YUKIHIKO ET AL) 24 January 2002 (2002-01-24) claim 1 -----	19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2004/014087

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 2,3;4-19(in part);20
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 2,3;4-19(in part);20

Present claims 2,3 and 4-19 in part, as far as they depend on claims 2 or 3 relate to an apparatus defined (inter alia) by reference to the following parameter: "positive test result" as further defined in claim 2.

The use of this parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful search impossible.

Furthermore, independent claim 20, relates to a catalyst supported on a material having a hollow cylindrical configuration which is defined among others by the parameter ratio of the tube diameter to the outside diameter 'of the hollow cylinder!'. Since no tube is defined/ mentioned in said claim the use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. The lack of clarity is such as to render a meaningful search impossible.

Consequently, the search has been restricted to claims 1,4-19 as far as they depend on claim 1.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

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